

Source Category Survey: Thermal Process
Phosphoric Acid Manufacturing Industry

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Source Category Survey: Thermal Process Phosphoric Acid Manufacturing Industry

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Thermal Process Phosphoric Acid
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1.0 SUMMARY

This Source Category Survey Report presents information gathered on processes, pollutants and control equipment for the thermal process phosphoric acid manufacturing industry. This industry manufactures phosphoric acid from elemental phosphorus, water, and air. This source category is a subpart of Standard Industrial Classification (SIC) code 2874.

There are 20 plants in the United States which produce thermal process phosphoric acid. These plants are located in 14 states rather evenly distributed across the country. In 1978, 627,300 Mg (691,500 tons) of 100 percent P_2O_5 were produced; there were 23 plants operational that year. Thus, average plant production is 27,300 Mg (30,100 tons) of 100 percent P_2O_5 per year.

Nearly 50 percent of all thermal process acid is used in detergent manufacturing. Although this market has now stabilized, it had been decreasing at the rate of 10 percent per year since 1970 due to the reduction of phosphates in detergents. Thermal process phosphoric acid is also used in beverages, food, dentrifices, metal treating, and fire control.

The major components of thermal process phosphoric acid production are: (1) combustion of elemental phosphorus with oxygen to produce phosphorus pentoxide and (2) hydration of the phosphorus pentoxide fume to produce the product acid. The production of elemental phosphorus was not considered in this report because it is not produced at the same location as the acid and because it is used for products in addition to phosphoric acid. The purification of thermal process acid, as required to meet food grade specifications, was overviewed.

The main pollutant from the thermal process is particulate, in the form of acid mist. Typical State Implementation Plan (SIP) particulate regulations for new plants are expressed by the equation:

$$E = 4.1 p^{0.67}$$

where E = allowable particulate emissions, in lb/h, and

p = process weight rate, in tons/h.

Typical plant emissions were calculated to be 2.6 kg/h (5.73 lb/h).

Other pollutants emitted include: nitrogen oxides from the combustion chamber, hydrogen sulfide from acid purification, and trace metals (specifically arsenic) as constituents of the phosphoric acid. These emissions are estimated to be minor; the arsenic emissions, for example, have been calculated to be less than 0.1 g/h (0.002 lb/h).

The recommended method for sampling phosphoric acid mist is a slightly modified version of EPA Reference Method 5. This method, as well as suggested analysis methods, are described in detail in Section 7.2.

Technology is available for control of acid mist. The equipment used extensively by the industry (to recover phosphoric acid and to control air pollution) includes: packed towers, scrubbers, fiber mist eliminators, and wire mesh contactors. All plants use a combination of control equipment, with typical recovery efficiency estimated to be over 99 percent. The best available control technology (BACT) is a packed tower or scrubber with some form of fiber mist eliminator or wire mesh contactor.

The information gathered in this survey indicates that a New Source Performance Standard (NSPS) should not be developed for the thermal process phosphoric acid industry. The main reasons for this recommendation are: (1) no increase in capacity at existing plants or construction of new plants is anticipated in the next 5 years, and (2) BACT will be utilized (for the purpose of product recovery) even if an NSPS is not developed. Even if a plant is built in the next 10 years, the air quality impact will be negligible.

2.0 INTRODUCTION

The authority to promulgate standards of performance for new sources is derived from Section 111 of the Clean Air Act. Under the Act, the Administrator of the U.S. Environmental Protection Agency is directed to establish standards relating to the emission of air pollutants and is accorded the following powers:

1. Identify those categories of stationary emission sources that contribute significantly to air pollution and which could be reasonably anticipated to endanger the public health and welfare;
2. Distinguish among classes, types, and sizes within categories of new sources for the purpose of establishing standards; and
3. Establish standards of performance for stationary sources which reflect the degree of emission reduction achievable through application of the best system of continuous emission reduction, taking into consideration the cost, energy, and environmental impacts associated with such emission reduction.

The term "stationary source" means any building, structure, facility, or installation which emits or may emit any air pollutants. A source is considered new if its construction, reconstruction, or modification is commenced after publication of the proposed regulations. Modifications subjecting an existing source to New Source Performance Standards (NSPS) are defined in 40 CFR Part 60.14.¹ Modifications include any physical change in the source or change in methods of operation which results in an increase in the amount or change in type of air pollutants emitted. Reconstructions subjecting an existing source to these standards are defined in 40 CFR Part 60.15 as "replacement of components of an existing facility to such an extent that the the fixed capital cost of the new components exceeds 50 percent of the fixed capital cost that would be required to construct a comparable entirely new facility" ²

Thermal process phosphoric acid manufacturing was recently included on a priority list of major source categories for which new source

standards should be developed.³ This source category survey was performed to determine if development of an NSPS for the thermal process phosphoric acid manufacturing industry is justified and to identify what processes and pollutants, if any, should be subject to regulation. Information about processes, air pollutants, and control equipment was gathered as follows:

1. Process and emission data were collected from literature searches and contacts with state and local air pollution control agencies.
2. Two thermal process phosphoric acid plants were visited to develop an understanding of manufacturing processes and to collect data on operating air pollution control equipment.
3. Representatives of industry, government agencies, trade associations, and control equipment vendors were contacted to gather information on thermal process phosphoric acid production and projected industry expansion.

Phosphoric acid is manufactured by two distinct processes: (1) the thermal process and (2) the wet process. The thermal process involves the burning of elemental phosphorus to form phosphorus pentoxide which is then hydrated. The wet process, on the other hand, consists of the treatment of phosphorus-containing rock with sulfuric acid.

Thermal process and wet process phosphoric acid differ in their degree of purity and hence serve different markets. Thermal process acid is low in impurities and is used primarily as an intermediate in the production of detergents, water builders, food additives, and animal feed. It is also used in fertilizer, metal treatment, and dentifrices. Although thermal process acid could be used for virtually all phosphoric acid requirements, it is used only when high purity acid is required because the production of elemental phosphorus is energy intensive and expensive. Wet process phosphoric acid, which is less expensive to produce, is used in markets where less purity is acceptable, primarily in the production of fertilizer. Wet acid impurities include fluorides, arsenic, calcium, iron, vanadium, aluminum, and sulfates.⁴ The thermal process is a more efficient method for using lower grade rock than the wet process. Presently, thermal process phosphoric acid comprises less than 9 percent of the total phosphoric acid produced in the United States.⁵ Methods to remove impurities in wet process acid are being

developed, and it is possible that wet process acid may expand into the thermal process market at some time in the future.^{6,7}

Historically, the thermal process production of phosphoric acid has developed from a one-step process to a two-step process. In the one-step process, phosphorus-containing rock is treated in an electric or blast furnace to produce elemental phosphorus vapor. The phosphorus vapor is passed directly, without cooling, to a combustion chamber where it is burned to produce phosphorus pentoxide (P_4O_{10}). It is then hydrated in an absorption tower to form phosphoric acid.

All thermal process phosphoric acid is currently produced by a two-step process. The first step consists of reduction of the phosphorus-containing rock in an electric furnace to produce liquid elemental phosphorus, P_4 . The second step consists of burning the elemental phosphorus with air in a combustion chamber at 1700°C to 2800°C.⁸ The resultant phosphorus pentoxide is hydrated with water and weak phosphoric acid until the desired strength of the final phosphoric acid is reached.

Presently, the first and second steps of the two-step process are performed at two separate locations, because the shipment cost of elemental phosphorus is less than that for phosphoric acid.^{9,10} (Four tons of phosphoric acid correspond by weight to one ton of phosphorus.)⁷ The elemental phosphorus is produced (first step) at the source of the phosphorus-containing rock. Although phosphorus-containing rock is primarily mined in Florida, rock from Tennessee and several western states is particularly suitable for elemental phosphorus production. Phosphoric acid is produced (second step) from elemental phosphorus at plants that serve local and regional markets.

The portion of the thermal process phosphoric acid manufacturing industry considered for the development of an NSPS is only the second step of the two-step process. Specific details on the air pollutant emission sources of the second step are documented in Chapter 4.

3.0 CONCLUSIONS AND RECOMMENDATIONS

3.1 CONCLUSIONS

1. In 1978, the total national production of thermal process phosphoric acid was 627,300 Mg (691,500 tons).⁵ During the period of 1978 to 1985, the national production is expected to increase at an average annual growth rate of less than 2 percent.

2. No increase in capacity at existing plants or construction of new plants is anticipated in the next five years.

3. The primary pollutant from the thermal process is particulate in the form of phosphoric acid mist. Other pollutants emitted in the process are: nitrogen oxides from the combustion chamber, hydrogen sulfide from acid purification, and trace metal constituents of the phosphoric acid mist.

4. The health effects of phosphoric acid mist are much less than those of other acid mists (e.g., sulfuric acid mist, nitric acid mist). The Threshold Limit Value (TLV) for noticeable but not uncomfortable effects of exposure to phosphoric acid is 1 mg/m^3 of air sampled (for an 8-hour time period).

5. Control technology is available for particulate (phosphoric acid mist) pollution control. There are no uncontrolled plants in the United States because the major pollutant, phosphoric acid mist, is valuable enough to justify the cost of a high degree of recovery.

6. Emission data are available for most plants. Based on data supplied by state regulatory agencies, emissions from plants average 60 percent below state allowable limits.

7. The standard method for evaluating emissions of particulate is a slightly modified version of EPA Reference Method 5.¹¹ The major revisions are: (1) removal of the filter support and filter and (2) use of 250 ml and 150 ml of deionized water in the first and second impingers in place of 200 ml distilled water in each impinger. This modified method is described in detail in EPA Publication No. AP-48.¹²

3.2 RECOMMENDATIONS

It is recommended that an NSPS not be developed at this time for the thermal process phosphoric acid industry. A standard would have no air quality impact for the following reasons:

1. No facilities are expected to be covered by the standard in the next five years. Growth of the industry is not likely. The industry is currently operating at approximately 50 percent of full production capacity. Existing capacity is sufficient to meet increased demand. No process changes are anticipated. Equipment life of major components is estimated to be 15 to 30 years. No plants are currently under construction, and no company indicated specific plans for new plant construction or expansion of existing capacity.^{13,14}

2. Best available control technology (BACT) will be utilized to recover product even if an NSPS is not promulgated. All existing plants use some form of control equipment with typical particulate control efficiency estimated to be over 99 percent. Allowable particulate emissions, under State Implementation Plans (SIP), from a typical plant are calculated to be 2.6 kg/h (5.73 lb/h) or 20.6 Mg/yr (22.7 tons/yr). On the average, actual particulate emissions were calculated to be 60 percent below SIP regulations. Even if a thermal process plant is built in the next 10 years (e.g., to serve the need for phosphoric acid in a specific region), the impact of an NSPS will be negligible.

4.0 INDUSTRY DESCRIPTION

4.1 SOURCE CATEGORY

The source category considered in this report is the manufacture of thermal process phosphoric acid from elemental phosphorus. This category is a subpart of the Standard Industrial Classification (SIC) code 2874. It is also specified by National Emissions Data System (NEDS) Source Classification Codes (SCC) 3-01-017-01 and 3-01-017-99, with emission factors in units of tons of phosphorus burned and tons of phosphoric acid produced, respectively. An alternative name for the thermal process is the phosphorus burning process.

There are 20 plants in the United States which currently produce phosphoric acid from elemental phosphorus (see Table 4-1). These plants are located in 14 states rather evenly distributed across the country. The number of phosphoric acid plants has been decreasing in recent years (see Table 4-2). Since 1968, nine plants have closed; two plants have opened; and at one plant, capacity has doubled.

In addition to a decrease in the number of thermal phosphoric acid plants, there has been a decrease in the utilization of capacity. The industry ran at an average of 64 to 68 percent of capacity in 1975 and now is running at 50 percent of capacity. Capacity utilization is expected to deteriorate further to 44 to 49 percent by 1982, assuming there are no plant closures.^{15,16,17}

Two factors which tend to reduce the growth in this industry are the increased cost of elemental phosphorus (resulting from increased electrical power costs) and the reduction of the phosphate content of detergents.

Thermal process phosphoric acid is used as a phosphorus carrier in markets where high purity acid is required. The largest markets for the acid are water builders and detergents. Other markets include: foods, beverages, pet foods, and dentifrices; metal treatment; fire control; and miscellaneous uses.^{15,18} The markets of thermal process phosphoric acid are very well established. Table 4-3 lists the most common grades of

TABLE 4-1. THERMAL PROCESS PHOSPHORIC ACID MANUFACTURERS, 1980

Company	Location
FMC Corporation	Newark, California Lawrence, Kansas Carteret, New Jersey
Hooker Chemical Company	Jeffersonville, Indiana Columbia, Tennessee Miller (Dallas), Texas
Hydrite Chemical Company	Milwaukee, Wisconsin
Mobil Chemical Company	Fernald, Ohio Charleston, South Carolina
Monsanto Company	Long Beach, California Augusta, Georgia Trenton, Michigan Carondolet (St. Louis), Missouri Kearney, New Jersey
Stauffer Chemical Company	Richmond, California South Gate, California Chicago, Illinois Chicago Heights, Illinois Morrisville, Pennsylvania Nashville, Tennessee

TABLE 4-2 NUMBER OF THERMAL PROCESS PHOSPHORIC ACID PLANTS,
1968 TO 1980^a

Date	No. of plants
1968	27
1975	26
1978	23
1980	20

^aSources: references 12 and 16 and telephone contacts with industry.

TABLE 4-3. GRADES OF PHOSPHORIC ACID¹⁸

Grade	Concentration
Technical	50%, 75%, 85% H_3PO_4
Food	75%, 80% H_3PO_4
USP (chemical)	10%, 85% H_3PO_4
90%	65% P_2O_5
100% acid	72% P_2O_5
105% acid	76% P_2O_5
Commercial	54% P_2O_5

phosphoric acid produced. All food grade acid is treated for removal of heavy metals (such as arsenic and lead) in order to meet strict food codes.¹⁹ More than 200 user-specific phosphate products may be produced by a single phosphoric acid plant. The most common phosphate compounds and their corresponding uses are summarized in Table 4-4.

4.2 INDUSTRY PRODUCTION

The national production of thermal process phosphoric acid increased steadily from 1940 to 1970 (see Figure 4-1).^{5,12} In the past decade, however, production has been decreasing an average of about 5 percent per year. As indicated in Figure 4-1, the 1978 production of thermal process acid was 627,300 Mg (or 691,500 tons) as 100 percent P_2O_5 .

The decrease in production has been caused mostly by a weakening market for phosphorus in detergent and water builders; approximately 50 percent of all thermal process acid produced is used in the detergent market.^{15,18} The use of phosphates in detergents has been declining at approximately 10 percent per year since 1970 as a result of evidence that detergent phosphates accelerate undesirable eutrophication in water bodies. Regional legislation requiring reduced phosphates in detergents has resulted in the development of nonphosphate or reduced-phosphate detergent products. In 1968 and 1969 the average phosphorus content of solid home laundry detergents was 13 percent; solid detergent today contains an average of less than 5 percent phosphorus.²⁰

Other smaller markets for thermal process phosphoric acid have been steady or slowly increasing in the past decade, compensating for the dramatic decline in the detergent market. Food, beverage, pet food, and dentifrice markets, which presently use 16 percent of the thermal process phosphoric acid in the United States, are becoming increasingly mature. Their projected growth rate for the next five years ranges from 1 to 4 percent. Use of acid for treatment of metal surfaces (primarily for aluminum polishing and phosphatizing), which was growing at a rate of about 5 percent per year in the 1960's, is expected to decrease by 2 to 4 percent in the 1980's.¹⁵

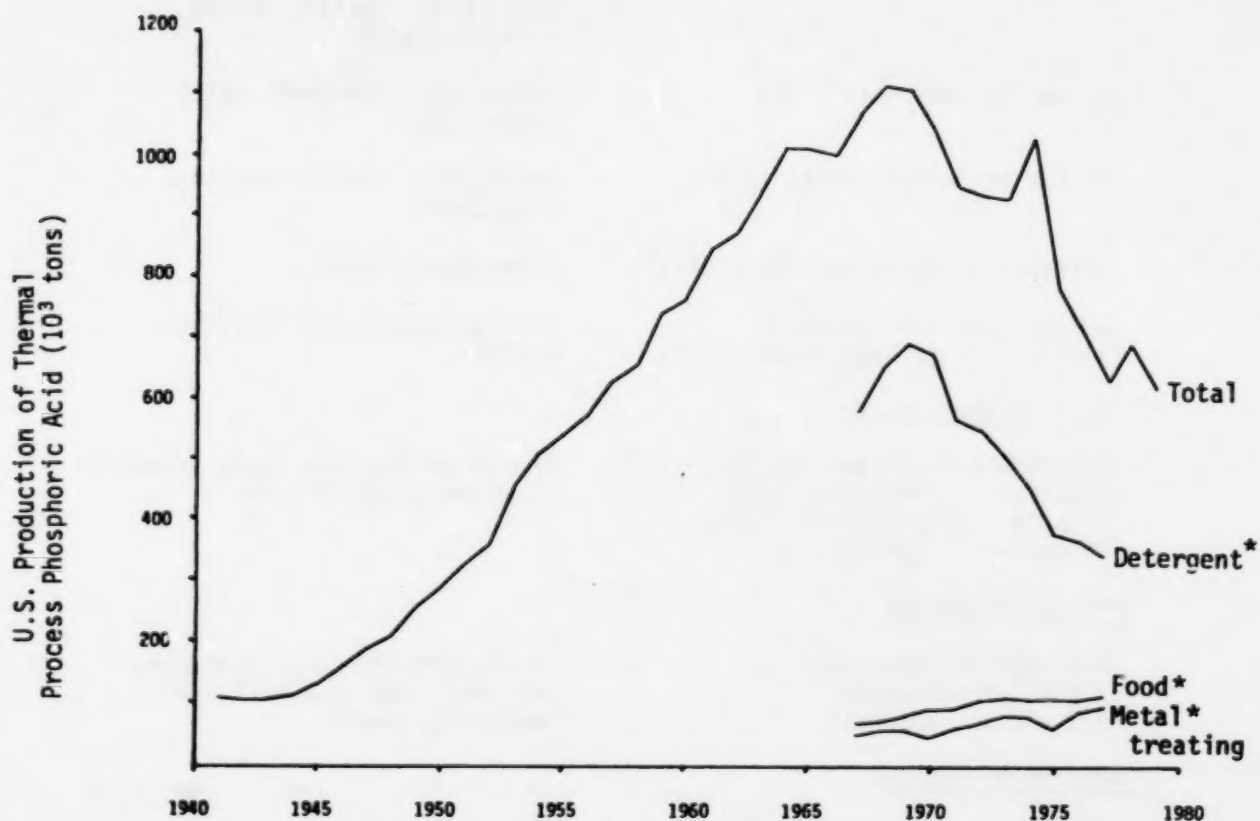
Although production of thermal process phosphoric acid has been decreasing for the past decade, total production of phosphoric acid has

TABLE 4-4. MAJOR PHOSPHORIC ACID PRODUCTS AND THEIR USES^{4,7,8,18}

Product	Uses
<u>Sodium phosphates</u>	
Monosodium phosphate (MSP) ^a	Buffer in acid-type cleaners.
Disodium phosphate (DSP)	Water treatment, dishwasher detergents, medicine, food processing, textile dyeing, ceramic glazes.
Trisodium phosphate (TSP)	Heavy duty detergent, water softening.
Sodium tripolyphosphate (STPP)	Detergents, clay processing, elastomers.
Tetrasodium pyrophosphate (TSPP) ^b	Detergent builder.
Sodium aluminum phosphate Sodium acid pyrophosphate (SAPP)	Baking powders and leavening agents.
<u>Potassium phosphates</u>	
Monopotassium phosphate (MKP) Dipotassium phosphate (DKP) Tripotassium phosphate (TKP) Potassium polyphosphates	Liquid detergents, dairy products, elastomers, antifreeze.
<u>Calcium phosphates</u>	
Monocalcium phosphate Dicalcium phosphate Tricalcium phosphate	Foods, dentifrices, beverages, including baking powders and leavening agents.
<u>Ammonium phosphates</u>	
Fluid	Fertilizers, livestock feeds, fire control.
Solid	Fire control, foods.
<u>Direct Acid</u>	Metal surface treatments, foods, refractories, beverages, catalysts.

^aMade by treating phosphoric acid (orthophosphoric) with soda ash.

^bMade by calcining anhydrous disodium orthophosphate.



*Thermal process phosphoric acid production applied to the specific market.

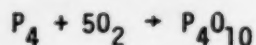
Figure 4-1. Historical production of thermal process phosphoric acid.^{5,12}

been increasing. This increase has been caused by the increase in production of wet process phosphoric acid (see Figure 4-2), which is used largely in the production of agricultural fertilizers.⁵ Wet process acid is less expensive to produce because it uses phosphate rock directly rather than elemental phosphorus, the energy-intensive raw material used in the thermal process. In 1978, energy accounted for approximately 66 percent of the total cost of producing elemental phosphorus.¹⁵ Sharp increases in the cost of energy have stimulated interest in substituting wet acid for thermal acid in some products. Historically, however, most U.S. producers have determined that the high purity acid can be produced more economically using thermal process acid than purified wet process acid.

No new thermal process plants are expected to be built in the next 5 years. If a plant were built in 5 to 10 years, it would most likely be small-to-medium size and would serve the demand for phosphoric acid in a specific location.^{13,14}

4.3 PROCESS DESCRIPTION

Figure 4-3 presents an overall flow diagram for the production of thermal process phosphoric acid and subsequent acid purification. The raw materials for acid production are: elemental phosphorus, air, and water. Elemental phosphorus is commonly shipped by tank car (as a liquid, under water) to the plant from an elemental phosphorus production plant.¹² Elemental phosphorus is transferred from a storage tank to a combustion chamber at typical feed rates of 4 to 20 liters/min (1 to 5 gal/min).²¹ In the combustion chamber, the phosphorus combines with oxygen to form phosphorus pentoxide (P_4O_{10}) by the combustion reaction:



Combustion takes place at 1650°C to 2760°C (3000°F to 5000°F).⁷ The combustion chamber is usually built of water-jacketed stainless steel, brick-level or graphite blocks.²² The resulting phosphorus pentoxide particles form a dense fume.²³

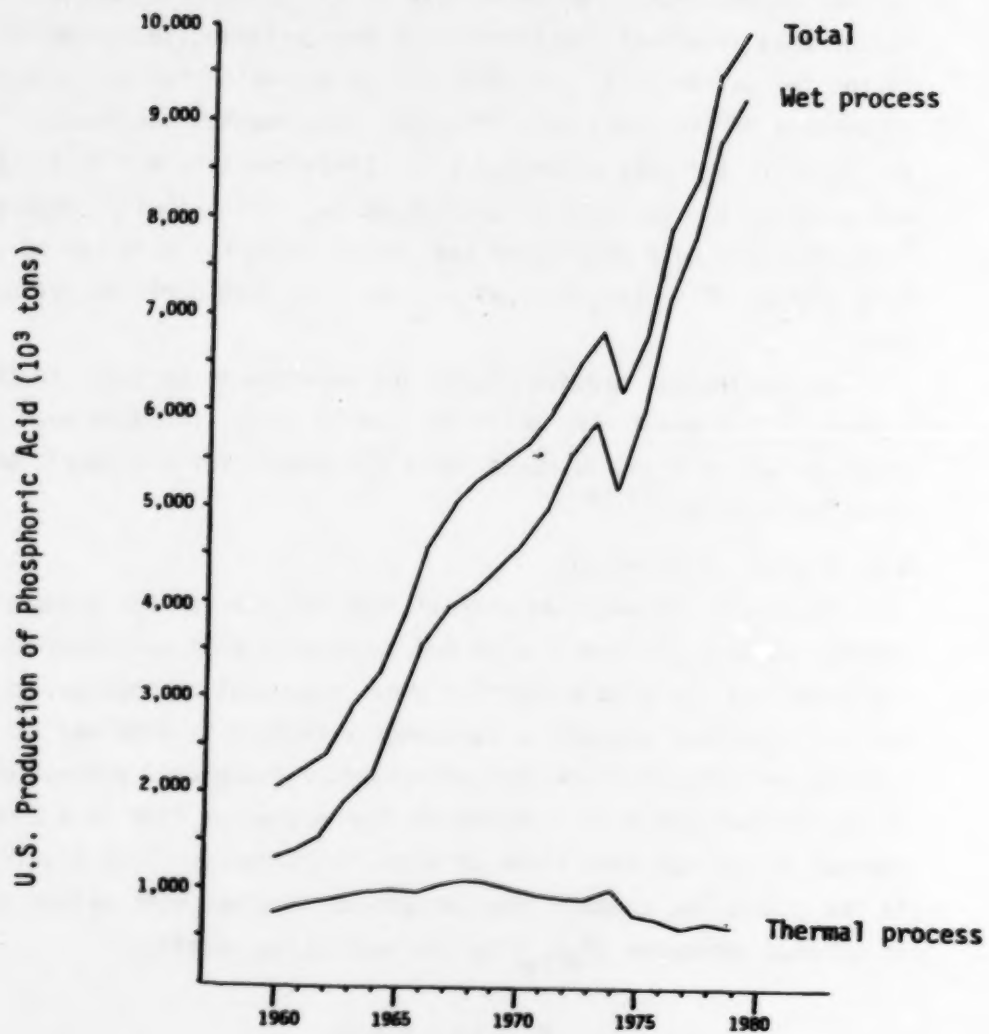


Figure 4-2. Production of phosphoric acid (total, wet process, and thermal process).⁵

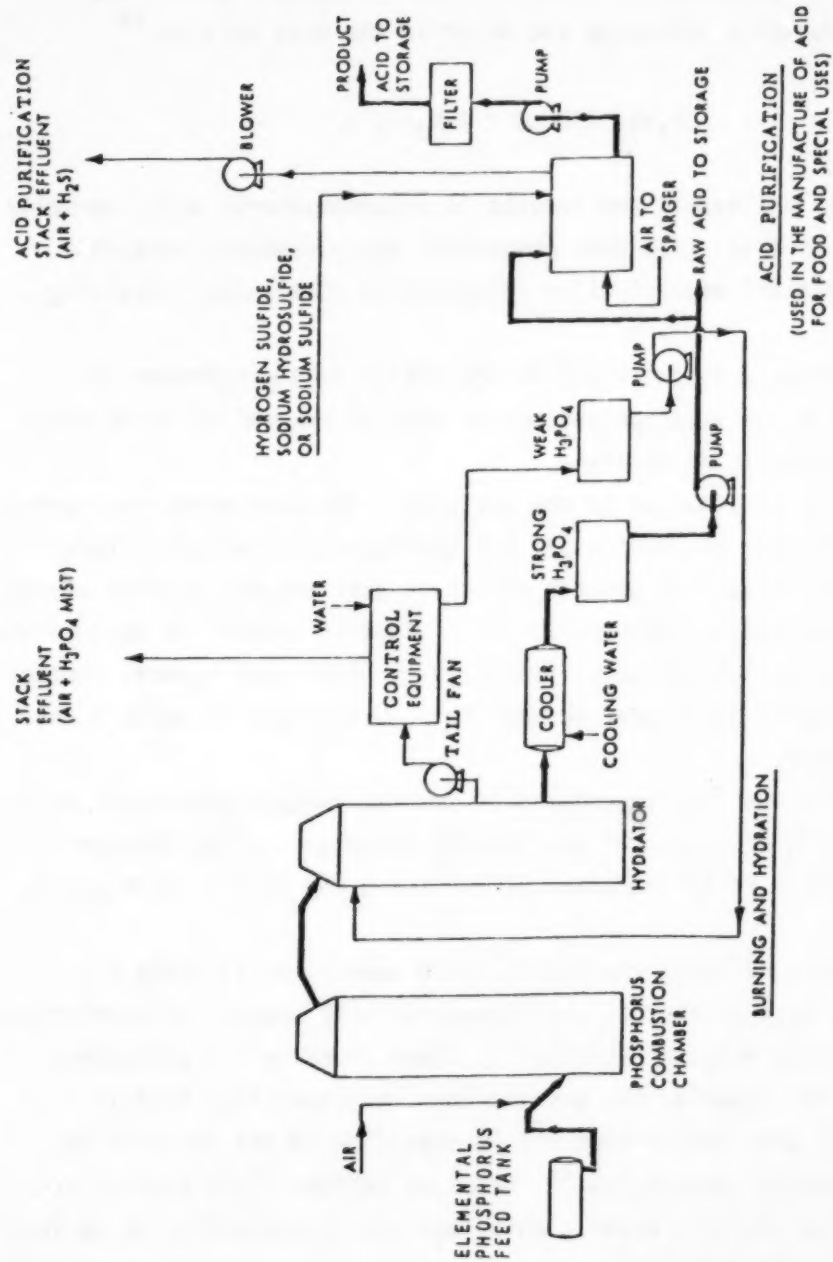
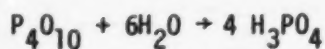


Figure 4-3. Flow diagram for typical thermal process phosphoric acid plant.^{12,21}

The phosphorus pentoxide passes to the hydrator where it is contacted with water and/or an aqueous solution of weak phosphoric acid. The reaction of phosphorus pentoxide and water in the weak acid is:²⁴



This reaction is exothermic and results in orthophosphoric acid, normally called phosphoric acid. (In some processes, the phosphorus pentoxide fume may be contacted with alkaline solutions to form salts containing phosphates.)

The product acid is drained from the bottom of the hydrator to storage. An acid purification process is used if removal of these heavy metals such as arsenic is desired.

Acid mist is also formed in the hydrator. The acid mist, unabsorbed phosphorus pentoxide, and excess air are contacted with water to form weak acid. This collection process serves to both enhance product recovery and reduce air pollution emissions. The collection process is accomplished by industry in a variety of ways; typically, a plant uses several control devices (see Chapter 6) to agglomerate the particles and to capture the liquid particulate.

The yield of the overall process of thermal process phosphoric acid manufacturing is high. Loss of any form of phosphoric acid, through leaks in the system or to the stack effluent (in the form of acid mist), is costly.

Typical stack effluent characteristics are summarized in Table 4-5. Phosphoric acid mist emitted to the atmosphere will contain concentrations of trace impurities which are similar to those found in the phosphoric acid product. For example, the arsenic level of unpurified acid is approximately 11 ppm; this varies widely depending on the ore used to produce the elemental phosphorus.²⁵ Based on typical plant particulate emissions (see Chapter 5), arsenic emissions can be calculated to be less than 0.1 g/h (0.0002 lb/h).

As indicated in the previous discussion, the major source of emissions to the atmosphere is the exit of the control equipment. Other pollution sources are the combustion chamber and the acid purification system (see

TABLE 4-5. TYPICAL STACK EFFLUENT CHARACTERISTICS^{12,21,26}

Characteristic	Typical value
Chemical composition	H ₃ PO ₄ , H ₂ O, NO _x , air
Moisture content	10 to 60 percent ^a
Opacity	0 to 100 percent
Particle density	1.57 to 1.68 g/cm ³
Particle size	0.4 to 2.6 microns
Mass median diameter	1.6 microns
Toxicity - TLV ^b	Irritant; 1.0 mg/m ³ ^c
Solubility	Soluble in water; decomposes in alcohol
Stack flow rate	1.6 to 14.3 m ³ /s (3,400 to 30,200 scfm) 900 to 4,100 m ³ /Mg product (35,000 to 160,000 scf/ton product) 7.1 m ³ /s (15,000 acfm) ^d
Stack temperature	60°C (140°F) ^d
Stack height	23 m (75 ft) ^d
Stack diameter	1.2 m (4 ft) ^d

^aUsually in the range of 40 to 50 percent.¹²

^bTLV = Threshold Limit Value.

^cNot to be exceeded for an 8-hr period.²⁶

^dAverage from NEDS printout (11/13/79).

Figure 4-1). High temperature combustion is conducive to formation of nitrogen oxides. The quantity of nitrogen oxides depends on flame temperature, residence time, and excess air. Nitrogen oxides are only a minor pollution problem in the thermal process phosphoric acid industry.¹²

Acid purification is a separate process to remove heavy metals (e.g., arsenic) to meet food grade specifications. Hydrogen sulfide (H_2S) is the emitted pollutant of this process. Pollution control for this process is commonly used and relatively inexpensive. The least expensive and most commonly used method vents the exhaust gases from the acid purification plant to the phosphorus furnace; this incinerates the H_2S to form SO_2 . Another method uses sprays of weak solutions of soda ash.¹² Most phosphoric acid plants have acid purification systems and are not reported to have a pollution problem. One data source reports hydrogen sulfide concentrations in the range of 10 to 2500 ppm for short periods of time.¹²

5.0 AIR EMISSIONS

5.1 PLANT AND PROCESS EMISSIONS

Emission test data for specific plants were requested from state and local control agencies, individual plants, and pollution control equipment vendors. Additional emission data were obtained from EPA's National Emissions Data System (NEDS), EPA Publication No. AP-48, and other literature sources.^{12,26,27}

Thermal process phosphoric acid plants emit particulates, mainly in the form of acid mist, and trace amounts of nitrogen oxides (NO_x) and hydrogen sulfide (H_2S). Acid mist is formed in the thermal process by gas cooling and by water/acid addition.¹² Only particulate is considered to be a significant emission (see Chapter 7).

Table 5-1 shows estimated particulate emissions from a typical thermal phosphoric acid plant and the data used in the calculations. Average plant production rate was calculated by dividing total 1978 U.S. production of P_2O_5 by the number of plants in operation that year. This production rate (in tons $\text{P}_2\text{O}_5/\text{yr}$) was converted to an average plant phosphorus burning rate (tons P/h). The typical burning rate is used in the typical process weight equation:

$$E = 4.1 p^{0.67}$$

where E = allowable particulate emissions, in lb/h, and
p = process weight rate, in tons P/h

This typical process weight rate equation is applicable to 10 of the 20 operational plants in the U.S.

Data obtained from state agencies contacted in this survey indicated that phosphoric acid plants commonly emit less particulate than is allowed by SIP's. Using emission data provided by four state agencies it was determined that plants emit an average of 60 percent less particulate than is allowed by the state SIP's. Table 5-1 presents the actual emission level in addition to the allowable SIP level.

TABLE 5-1. PARTICULATE EMISSIONS FROM A TYPICAL THERMAL PROCESS
PHOSPHORIC ACID PLANT

<u>Basis</u>	
Production rate:	27,250 Mg P_2O_5 /yr (30,040 tons P_2O_5 /yr)
Process weight rate:	1.50 Mg P/h (1.65 tons P/h) 11,900 Mg P/yr (13,110 tons P/yr)
Operating rate:	330 working days/yr 7,290 h/yr
<u>Typical plant emissions (as 100% P_2O_5)</u>	
Uncontrolled:	1,040 kg/h (2,300 lb/h) 8,200 Mg/yr (9,100 tons/yr)
SIP:	2.6 kg/h (5.73 lb/h) 20.6 Mg/yr (22.7 tons/yr)
Actual:	1.04 kg/h (2.3 lb/h) 8.2 Mg/yr (9.1 tons/yr)

The average production for a thermal phosphoric acid plant is 27,250 Mg (30,040 tons) of 100 percent P_2O_5 per year. Average allowable emissions are 2.6 kg of P_2O_5 /h (5.73 lb/h). Applying a 60 percent reduction, the emissions from a typical plant are 1.0 kg of P_2O_5 /h (2.3 lb/h).

No uncontrolled plants exist in the United States because it is not profitable for the plants to lose the phosphoric acid mist to the atmosphere. Back calculating from a 99.9 percent control efficiency, uncontrolled emissions for a typical plant are 1,040 kg of P_2O_5 /h (2,300 lb/h) or 8,200 Mg of P_2O_5 /yr (9,100 tons/yr).

5.2 TOTAL NATIONAL EMISSIONS

Baseline nationwide emissions (calculated using process weight equations) are 412 Mg of P_2O_5 (454 tons/yr) or 52 kg of P_2O_5 /h (114 lb/h), if all 20 existing plants meet state regulations. By applying a 60 percent reduction, the actual total nationwide emissions are estimated to be 165 Mg of P_2O_5 /yr (182 tons/yr).

6.0 EMISSION CONTROL SYSTEMS

6.1 CONTROL APPROACHES

Control equipment is used by the industry for recovery of product as well as for air pollution control. It is difficult to determine where economic product recovery ends and control of air pollution begins. The equipment used extensively by the thermal process industry to recover phosphoric acid or to control emissions includes: packed towers, electrostatic precipitators, scrubbers, fiber mist eliminators, and wire mesh contactors.^{12,28,29} As indicated in Table 6-1, each of the 20 operational plants use an average of two types of equipment, and no operational plant uses an electrostatic precipitator.

The following paragraphs describe the characteristics of each device used for collecting acid mist. Criteria for selection of suitable control equipment are: (1) collection efficiency required for economic product recovery, (2) pressure drop across the control equipment, (3) capital and operating costs, (4) frequency of equipment maintenance and repair, and (5) particle size of the effluent to be collected.

6.1.1 Packed Towers

Packed towers (also called packed scrubbers) have been used in the industry for many years. Basically, a packed tower is a vertical vessel with packing material. The packing material, such as Raschig rings or coke, provides surface area for interaction of liquid and gas phases. Gas enters the bottom of the tower and is contacted countercurrently in the packed tower with water or dilute acid. Typical gas flow rates range from 0.9 to 2.0 m/s (3 to 6.5 ft/s), and packed material height ranges from approximately 1.2 to 2.4 m (4 to 8 ft). Packing should provide maximum surface area and minimum void area. Uniform gas distribution is also essential for optimum collection efficiency.²⁹

The collection efficiency of a packed tower is about 90 percent. Efficiencies of 98 percent and higher have been obtained by using two

TABLE 6-1. SUMMARY OF CONTROL EQUIPMENT APPLIED
TO OPERATIONAL PLANTS

Control equipment type	Number of operational plants with control equipment ^a
Pack tower	7
Scrubber	8
Cyclone separator	2
Fiber mist eliminators	11
Wire mesh contactors (Demister)	11

^aFor 20 operational plants listed in Table 4-1.

packed towers in series. A pressure drop of 30 in. W.G. might be expected through a system of two packed towers in series.

6.1.2 Electrostatic Precipitators

Electrostatic precipitators (ESP's) were used extensively by the Tennessee Valley Authority (TVA) in thermal process acid plants.⁹ Corrosion is the biggest problem with the application of ESP's in this industry.²⁹ Presently no ESP's are used at operational thermal process phosphoric acid plants.

The ESP operates at an approximate pressure drop of 0.12 kilopascal (kPa) (0.5 in. W.G.). The reported collection efficiency for six installations ranges from 96.3 to 99.9 percent.²¹ An installation of two ESP's in series achieved a collection efficiency of 99.15 percent.²⁹

6.1.3 Scrubbers

Wet scrubbers are widely used for acid mist collection and operate with high collection efficiencies. Water and/or weak acid is used as the scrubbing agent. Collection efficiency is directly related to pressure drop. Efficiency typically ranges from 98 to 99 percent.^{12,29}

Venturi scrubbers, an orifice type wet scrubber, are especially effective for the collection of particles characteristic of the acid mist. They also have lower operating costs than ESP's and some other control equipment if the collected sludge is disposed of without clarification.²⁹ However, the high cost of electric power to operate fans and to pump water may be a disadvantage for the use of venturi scrubbers in new applications. Pressure drops across the venturi scrubber have been reported in the range of 6.2 to 15 kPa (25 to 60 in. W.G.).^{21,29}

Some plants have installed a mist eliminator after the scrubber. This combination increases collection efficiency to greater than 99.9 percent.

6.1.4 Fiber Mist Eliminators

Glass fiber mist eliminators have been developing as a type of collection device since the late 1950's.^{30,31} This control equipment has been applied to various chemical processes, including sulfuric acid plants, thermal process phosphoric acid plants, chlorine plants, nitric

acid plants, and plants emitting ammonium chloride fume or bacteria particles.³¹

A mist eliminator consists of vertical elements in a vertical cylinder. Unclean gas enters at the top or side of the cylinder, and clean gas leaves the side or top. The eliminator has a drain at the bottom of the cylinder to outlet the collected weak acid.

Two criteria must be met to ensure effective operation of fiber mist eliminators: (1) the gas stream should not contain excessively large particles and (2) there should be uniform gas flow through the mist eliminator. The mist eliminator is frequently used after another type of control device.

Collection efficiency has been reported in the range of 95 to 99.98 percent on particles smaller than one micron, with pressure drops in the range of 1.2 to 5.0 kPa (5 to 20 in. W.G.).^{12,31}

6.1.5 Wire Mesh Contactors

Wire mesh contactors (or pads) are the newest type of control equipment for phosphoric acid mist. The wire mesh contactor was developed by Otto H. York, Inc. and FMC Corporation under the registered trademark of "Demister."³² The first commercial unit was operational in July 1964 and consisted of two stainless steel wire mesh contactors in series. This type of collection equipment is compact and has no moving parts. Collected acid drains by gravity to a tank.

Outlet mist loading is directly related to the pressure drop for a particular mesh material. The wire mesh contactor, like the fiber mist eliminator, is most suitable to applications where the unclean gas does not contain insoluble solids which might cause plugging of the wire mesh pads.

The design collection efficiency of the wire mesh contactor is 99.9+ percent. Pressure drop ranges from 5 to 10 kPa (20 to 42 in. W.G.).^{29,32}

6.2 ALTERNATIVE CONTROL TECHNIQUES

Several combinations of control equipment are used by the thermal process phosphoric acid manufacturing industry. The most widely used combination is some form of packed tower or scrubber with a fiber mist

eliminator or wire mesh contactor. This type of control system typically has a design efficiency of 99.9+ percent.

6.3 "BEST SYSTEMS" OF EMISSION REDUCTION

The most effective system (99.9+ percent) of emission control is probably the combination of a packed tower or scrubber with a form of fiber mist eliminator or wire mesh contactor. This type of control system, as indicated earlier, is the most frequently used system and has been installed most recently to replace other forms of control equipment (e.g., ESP's). In addition, it is economical to add these devices to existing equipment.

7.0 EMISSION DATA

7.1 AVAILABILITY OF DATA

The availability of emission data was determined through telephone and letter contacts to state and local control agencies as well as the individual thermal process phosphoric acid plants. The data available was for particulate emissions, except for a small amount of data on NO_x , HC, and CO provided by the State of California. Nineteen state and local agencies were contacted. All plants/companies (see Table 4-1) were contacted for specific process and emissions data. Particulate and nitrogen oxide emission data prior to 1968 for 25 plants are reported in EPA Publication No. AP-48.¹² These data are not included in this survey.

Typical plant and nationwide emissions were calculated using the method described in Chapter 5. Allowable emissions for a typical plant under an SIP were calculated to be 2.6 kg/h (5.73 lb/h); actual emissions from a typical plant were an average of 60 percent lower, or 1.04 kg/h (2.3 lb/h). Data provided by states and plants show that plant emissions range from 0.2 to 14 kg/h (0.43 to 30 lb/h).

Operating practices, including changes in the grade of acid produced, have little effect on emissions of acid mist.¹⁵ The acid mists are very hygroscopic; thus, visible emissions are readily noticeable if high collection efficiencies are not achieved.³³

7.2 SAMPLE COLLECTION AND ANALYSIS

7.2.1 Particulate

Particulate (phosphoric acid mist) emissions may be measured using EPA Reference Method 5 as described in 40 CFR 60, Appendix A¹¹ or EPA Reference Method 5 with slight modifications as described in detail in EPA Publication No. AP-48.¹² These modifications include: (1) removal of the filter and filter support; (2) use of 250 ml and 150 ml of deionized water in the first and second impingers, respectively, in place of 200 ml

of distilled water; and (3) termination of sampling before water entrainment occurs in the third impinger.

Two sample analyses methods are also described in detail in EPA Publication No. AP-48.¹² These are: (1) a spectrophotometric determination (i.e., colormetric method), as adopted by the Association of Official Analytical Chemists and (2) an American Chemical Society (ACS) acid-base titration method adapted for these samples. Both methods are specifically applicable to the samples collected using the modified EPA Reference Method 5 for effluents from thermal process phosphoric acid plants.

7.2.2 Opacity, Nitrogen Oxides, and Hydrogen Sulfide

EPA Reference Method 9 (as described in 40 CFR 60, Appendix A) is available for determination of visible emissions.¹¹ The plume from thermal process phosphoric acid plants usually contains high moisture content (40 to 50 percent moisture), and appropriate procedures (i.e., reading plume after steam dissipates) should be followed as described in the method.

EPA Reference Method 7 (described in 40 CFR 60, Appendix A) is available for the collection and analysis of nitrogen oxide emissions.

EPA Reference Method 11 (described in 40 CFR 60, Appendix A) could be used for determination of hydrogen sulfide content of emissions from the acid purification system. Some modifications might be necessary to convert this method to this source category.

8.0 STATE AND LOCAL EMISSION REGULATIONS

The following paragraphs provide information on pertinent state and local agency regulations. These data were compiled from (1) telephone contacts and letter requests to the specific agencies and (2) the Environment Reporter.³⁴

Thermal process phosphoric acid plants are in operation in 14 states (see Table 4-1). All 14 states have emission regulations for particulates and visible emissions (opacity). These regulations are summarized in Table 8-1. None of the states has developed any emission standards specific to new or existing thermal process phosphoric acid manufacturing plants; most state regulations categorize this source as an "industrial" or "manufacturing" process. Although six of the states regulate sulfuric acid mist, no state regulates phosphoric acid mist.

The majority of the states listed in Table 8-1 use the following process weight rate equations to establish allowable particulate emissions:

$$E = 4.0 p^{0.67} \quad p \leq 30 \text{ tons}$$

$$E = 55.0 p^{0.11} - 40 \quad p > 30 \text{ tons}$$

where E = allowable particulate emission rate, in lb/h

p = process weight rate, in tons/h

Several states have used the above equations to calculate emission limits for specific process weight rates. These states provide tables and/or graphs for determining allowable emissions. Other states have developed their own process weight rate tables and equations. The California South Coast Air Quality Management District (SCAQMD), for example, uses a table which requires lower emissions than the equations of the majority of the other states. An average sized plant (burning 1.65 tons of elemental phosphorus per hour) which would be allowed to emit 5.73 lb of particulate per hour using the above equations would be limited to emitting 4.86 lb of particulate per hour in the SCAQMD.

Most states with operating thermal process phosphoric acid plants limit opacity to 20 percent but allow deviations above this level for a small percentage of time in an hour or day.

All states that supplied allowable and actual emission data indicated that thermal process phosphoric plants were operating well within applicable

TABLE 8-1. SUMMARY OF STATE AIR POLLUTION REGULATIONS

	Particulate	Visibility	Air pollution regulation reference
California			
Bay Area	Equation Set 1 ^a	≤20, exception	Bay Area Air Control District Reg. IV, September 1977
South Coast	Process weight rate table 405, Type A	≤20, exception	Rules and Regulations South Coast Air Quality Management District, Reg. IV, September, 1977
Georgia	$E = 4.1p^{0.67}$	≤20, exception	Georgia Air Quality Control Rules, Chapter 391-3-1, November 1975
Illinois	Equation set 2	≤30, exception	Illinois Stationary Sources Standard; May 1979. Rule 201, 202, 1977.
Indiana	Equation set 1	≤40, exception	Indiana Air Pollution Control Regulations, APC-3, May 1979
Kansas	Equation set 1	---	Kansas Air Pollution Control Regulations, Section 28, January 1974
Michigan	Equation set 1	≤20, exception	Michigan Administrative Rules for Air Pollution Control Regulations, Section 28, January 1974
Missouri	Equation set 1	≤20, exception	Missouri Air Pollution Control Regulation, 10 CSR 10-5, December 1979

TABLE 8-1. SUMMARY OF STATE AIR POLLUTION REGULATIONS
(continued)

	Particulate	Visibility	Air pollution regulation reference
New Jersey	≤ 0.2 g/dscf or 99% reduction	≤ 20 , exception	New Jersey Regulations on Air Pollution from Manufacturing Processes, Subchapter 6, May 1977
Ohio	Equation set 1	≤ 20 , exception	Ohio Particulate Matter Standards, September 1978
Pennsylvania	≤ 0.2 g/dscf or equation 3 ^d	≤ 20 , exception	Pennsylvania Standards for Contaminants, Section 123, July 1978
South Carolina	Equation set 1	---	South Carolina Air Pollution Control Regulations and Standards, Section 6, May 1978
Tennessee	Equation set 1	≤ 20 , exception	Tennessee Air Pollution Control Regulations, Chapter 1200-3, February 1977
Texas	Equation set 4 ^e	≤ 30 , exception	Texas Regulation 1: Control of Air Pollution From Visible Emissions and Particulate Matter, Section 131, May 1979
Wisconsin	Equation set 5 ^f	≤ 20 , exception	Wisconsin Air Pollution Control Rules, NR 154.11, May 1, 1977

^aEquation Set 1:
 $E = 4.1p^{0.67}$
 $E = 55p^{0.11-40}$
 $p \leq 30$ tons/h
 $p > 30$ tons/h
 E = allowable emission rate, in lb/h.
 p = process weight rate, in tons/h.

TABLE 8-1. SUMMARY OF STATE AIR POLLUTION REGULATIONS
(concluded)

^bThis equation alone is used for all existing equipment. New equipment is subject to the restrictions of both equations in Equation Set 1.

^cEquation Set 2:
 $E = 2.45p^{0.534}$ $p \leq 450$ tons/h
 $E = 24.8p^{0.16}$ $p > 450$ tons/h
 Existing equipment is subject to the restrictions of Equation Set 1.

^dEquation Set 3:
 $A = 0.76E^{0.72}$
 A = allowable emissions
 E = $F \times W$
 F = process factor, 6 lb/ton P burned for H_3PO_4
 W = production/charging weight

^eEquation Set 4:
 $E = 3.59p^{0.985}$ $p \leq 20$ tons/h
 $E = 25.4p^{0.287}$ $p > 20$ tons/h
 Further reductions are required if stack height is less than the standard effective stack height.

^fEquation Set 5:
 $E = 3.59p^{0.62}$ $p \leq 30$ tons/h
 $E = 17.31p^{0.16}$ $p > 30$ tons/h

^gMost states allow opacity to exceed restricted levels for brief periods per hour or day.

particulate regulations. On the average, the actual emissions of a plant were 60 percent below the allowable state emissions. Only two states reported any history of problems with any of their thermal process phosphoric acid plants.

Nitrogen oxides are a potential emission from the combustion chamber in the thermal process. No state has regulations which are directly applicable to thermal process phosphoric acid plants. Georgia has a regulation which applies to any nonfuel-burning equipment. For stack height less than 300 ft, the allowable emissions are:

$$E = 9300 (h_s/300)^3$$

where E = allowable NO_x emissions, in lb/h, and

h_s = stack height, in ft

Hydrogen sulfide emissions are generated in the acid purification unit of a thermal process plant. Three of the fourteen states have regulations for hydrogen sulfide emissions; the emission limits are 0.06 ppm, 0.03 ppm, and 0.08 ppm for the states of California (Bay Area), Missouri, and Texas, respectively. Each of the three state regulations specify periods of time (3 to 30 min.) for which the limit should not be exceeded.

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